Electroactive Polymers (EAP) Characterization Methods

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ABSTRACT

Electroactive polymers (EAP) are emerging as a new class of actuation materials being considered in a wide range of applications. Their large electrically induced strains (bending or extensional), low density, ease of processing, and mechanical flexibility offer advantages over traditional electroactive materials. However, before these materials can be properly exploited, their electrical and mechanical properties must be properly quantified. Two general types of EAP can be identified including wet (hydrated) and dry materials. The first type requires relatively low voltages (<10V) to achieve large bending deflections (more than 90°). This class usually needs to be hydrated and electrochemical reactions may occur. The second type of EAP involves electrostrictive and/or Maxwell stresses. These types of materials require large electric fields (>100MV/m) to achieve large extensional deformation (>4%). Some of the difficulties that are involved with the characterization of the properties of EAP include nonlinearity, large compliance (large mismatch with metal electrodes), non-homogeneity formed during processing, etc. In order for this technology to fully mature, the authors are developing characterization techniques to quantify their electroactive responses and material properties. This paper focuses on a new testing procedure for bending EAP. Results for ion exchange Flemion membranes are presented.

1. INTRODUCTION

Nafion®[1]and Flemion® [2] are membranes with fluorocarbon backbones and mobile cations (counter-ions). When a voltage (<10) is applied to a hydrated sample, the large ionic conductivity may promote electro-osmosis[3] and/or hydrolysis[4]. The former response manifests itself as a bending of the film towards the positive electrode (anode) and can be exploited in actuation applications[5]; while the latter is an undesired electrochemical reaction that consumes power and may damage the electrode by producing gas. Kanno et al.[6] have shown that the bending response of Pt -electroded Nafion (Na+ counter-ion) is complicated by relaxation processes. If a dc voltage is applied for sufficient time, the primary deflection will gradually return to its initial position. This phenomenon is thought to be due to the excess concentration of water near the cathode and its subsequent back-flux[7]. It is interesting to note that this behavior is not evident in Au –electroded Flemion (tetra-n-butylammonium counter-ion)[2]. The large size of the cation and its sluggish mobility may provide an explanation.

The large bending deflections, required hydration, and relaxation processes make electromechanical characterization difficult. This paper presents a technique for quantifying the electrically induced mechancial response of Au –electroded Flemion (tetra-n-butylammonium counter-ion). Similar electroactive polymers (EAP) such as polypyrrole[8] may be analyzed in similar fashion.

2.EXPERIMENTAL PROCEDURE

The samples investigated in this study were Au-Flemion with tetra-n-butylammonium as the counter-ion. The processing procedure was outlined previously by Oguro[2]. The dimensions of membranes were 0.2 mm thick, 4mm wide, and 20 mm long. Bending curvature and tip deflection were measured using a Sony XC-55 progressive scan CCD in conjunction with an IMAQ PCI-1407 (National Instruments) image acquisition board. Voltage was supplied by a DAQ AT-MIO card (National Instruments) and amplified using a Hewlett Packard HP 467A power amplifier. All measurements were computer controlled using a program written in LabView® 5 (National Instruments). Matlab® 5 (MathWorks) with Image Processing Toolbox

was used to analyze the data. A GS0-10 (Transducer Techniques) load cell with TM0-1 signal conditioning module (Transducer Techniques) was used to measure electrically induced tip force. Sheet resistance of Au electrodes as measured using a four point probe and Keithley 2001 high precision multimeter. The spacing between each probe was 2.5mm. Peel test was used to assess quality of adherence of electrode to the membrane.

3.RESULTS AND DISCUSSION

Good conductivity of the electrodes is essential for uniform bending of ion exchange membranes. The sheet resistance of the Au electrodes was found to increase from 0.2 ohms to 0.9 ohms when hydrated. This was probably due to swelling of the membrane as it sorbs water. Good adherence of the electrode to the membrane was demonstrated by firmly pressing Scotch® tape to the surface and then peeled off rapidly.

Figure 1 displays an image of a Flemion membrane submerged in de-ionized water. The scale was determined by counting the number of pixels along the dimensions of the rectangular part of the sample holder and comparing with its known size in millimeters. The scaling factor was then determined to be 0.15mm/pixel. The outline of the area traversed by the bending sample under the influence of applied 3.0V, 0.05 Hz cosine signal is marked on the image.
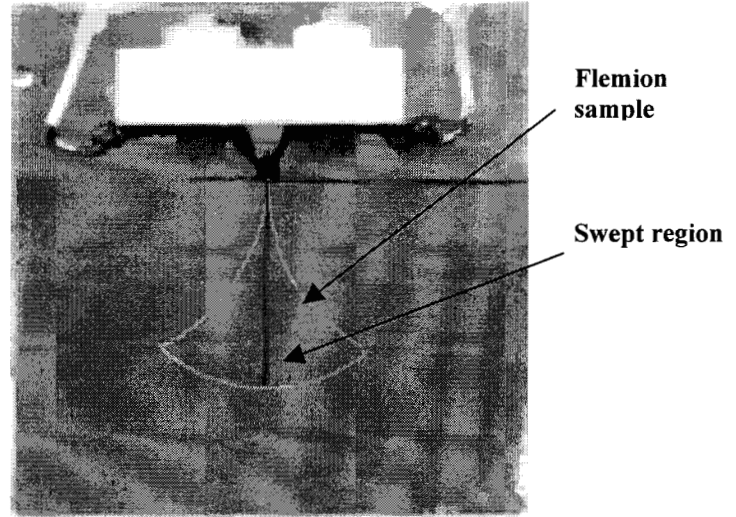
The plot in Figure 2 shows the swept region of Figure 1 with scaled units. The circles respresent pixel positions determined by an edge detection algorithm employing a Radon transform[9]. The sampling frequency (number of pictures taken per second) was 2 Hz. Least squares curve fitting resulted in analytic expression, y_1 and y_2, for the extreme bending deflections. An assymetry in the bending response is evident. The shaded area was calculated to be 125mm^2.

Figure 1. Image displaying electrically induced bending deformation of Flemion sample.

When a cantilevered beam subjected to pure bending is bent into an arc of a circle, the curvature, $1/R$, of the neutral surface can be expressed as

$$\frac{1}{R} = \frac{PL}{EI} ,$$ (1)

where P is a concentrated load located at the free end of the cantilever of length L. The 'stiffness' of the beam is proportional to the product of the elastic modulus E and moment of inertia I and is commonly referred to as the *flexural rigidity*. To a first approximation the bending curvature of the Flemion samples subjected to voltage of 3.0V, 0.05 Hz cosine wave can be assumed constant along its length. Figure 3 shows the two deflections, y_1 and y_2, fitted with circles of radii R_1 = 17.1mm and R_2 = -15.6mm. With appropriate values of elastic modulus and neglecting viscous forces of the surrounding water it is possible to estimate the induced tip force generated by a given voltage using equation 1.

There are a number of different ways to express the bending motion. Figure 4 shows tip delelection as a function of time as measured by (b) linear displacment from the y-axis, (c) angular displacment. It is also possible to monitor the change in curvature (Figure 4b).

The hysteresis between angualt tip deflection and applied voltage is shown in Figure 5 for 1.0V, 2.0V, and 3.0V at 0.05Hz. Figure 6 shows the response to a dc voltage applied at t=0 s. Both of these figures imply that the mechanism for deformation is sluggish and is probably due to the large size and low mobility of the tetra-n-butylammonium counter-ion. The relaxation process is quite different than that observed for Pt-Nafion (Na$^+$ counter-ion)[6].

Tip force was also measured. The sample was removed for water and 3mm of free end was in contact with load cell. A 5 V, 0.05 Hz cosine wave was applied. The sampling frequency was 1.0 Hz. From Figure 7 it is evident that the nominal value of force is quite small (~0.6mN peak).
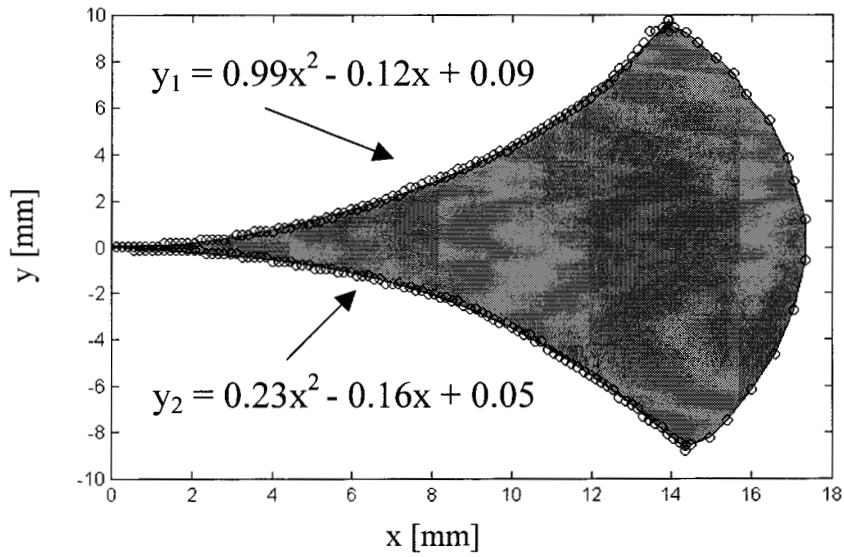

$$y_1 = 0.99x^2 - 0.12x + 0.09$$

$$y_2 = 0.23x^2 - 0.16x + 0.05$$

Figure 2. Bending response of Nafion to applied voltage of 3.0V ,0.05 Hz. The shaded region represents the swept area equla to 125mm^2.
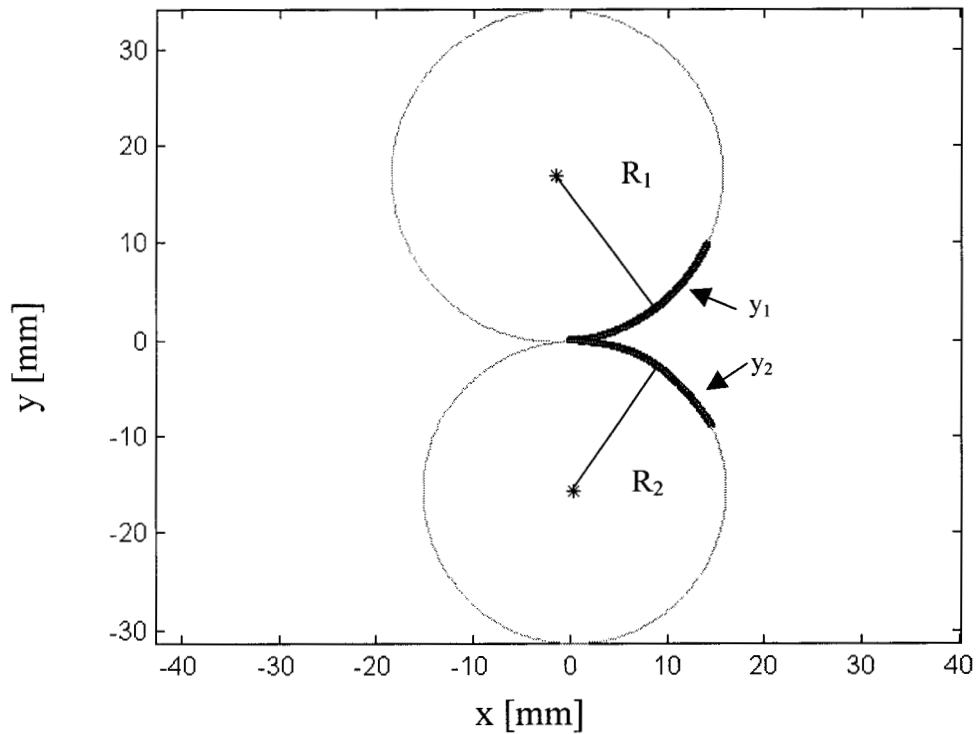

Figure 3. The bending response can be approximated as constant curvature, which simplifies modeling.
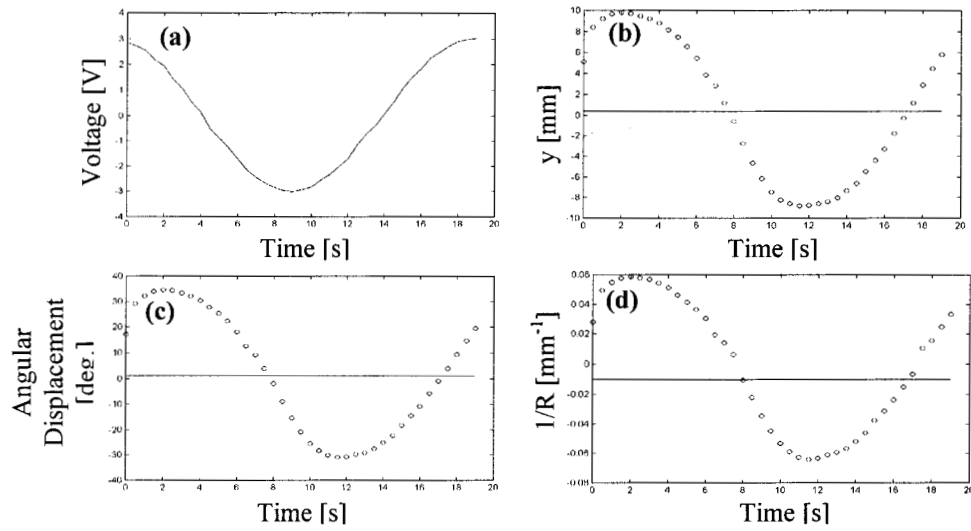
Figure 4. Bending response to (a) applied voltage can be quantified in a number of ways including: (b) displacement of tip from y-axis, (c) angular displacement of tip, (d) curvature. The horizontal line in the plots represents the initial displacement of the sample before voltage was
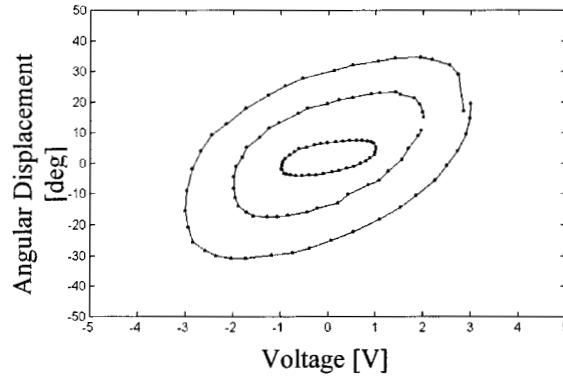

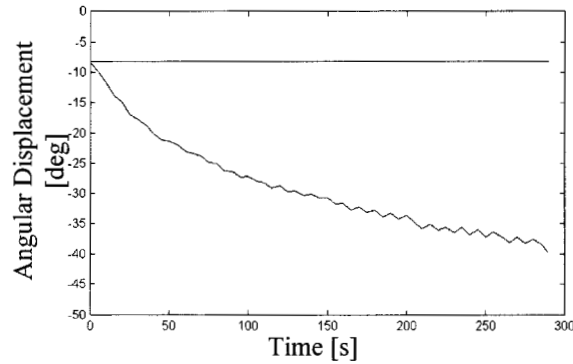Figure 5. Hysteresis of tip displacement for 1.0V, 2.0V, and 3.0V at 0.05Hz.

Figure 6. Tip displacement response to applied dc voltage of 2.0V. The horizontal line represents the initial deformation present before voltage applied.
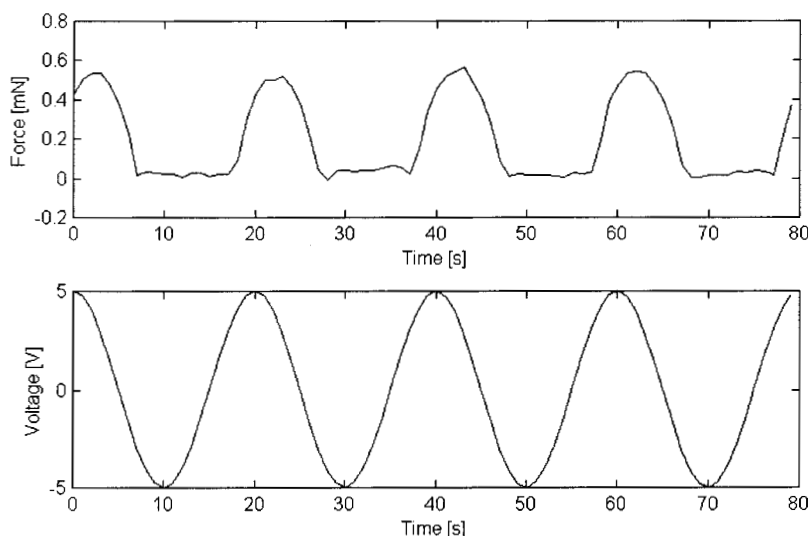
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Figure 7. Tip force and applied voltage

CONCLUSION

Bending EAP such as ion exchange membranes are difficult to characterize. In order for them to be accepted for applications it is necessary to quantify their behavior and develop suitable models. A new procedure for characterizing the bending response of electroactive polymers was presented.

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